

Direct Observations of the Real Structures of Crystals of Some Tetrahedrally Close-Packed Alloys

A High Resolution Electron
Microscopy Study

Lars Stenberg



Lund 1984



DIRECT OBSERVATIONS OF THE REAL STRUCTURES OF CRYSTALS
OF SOME TETRAHEDRALLY CLOSE-PACKED ALLOYS
A High Resolution Electron Microscopy Study

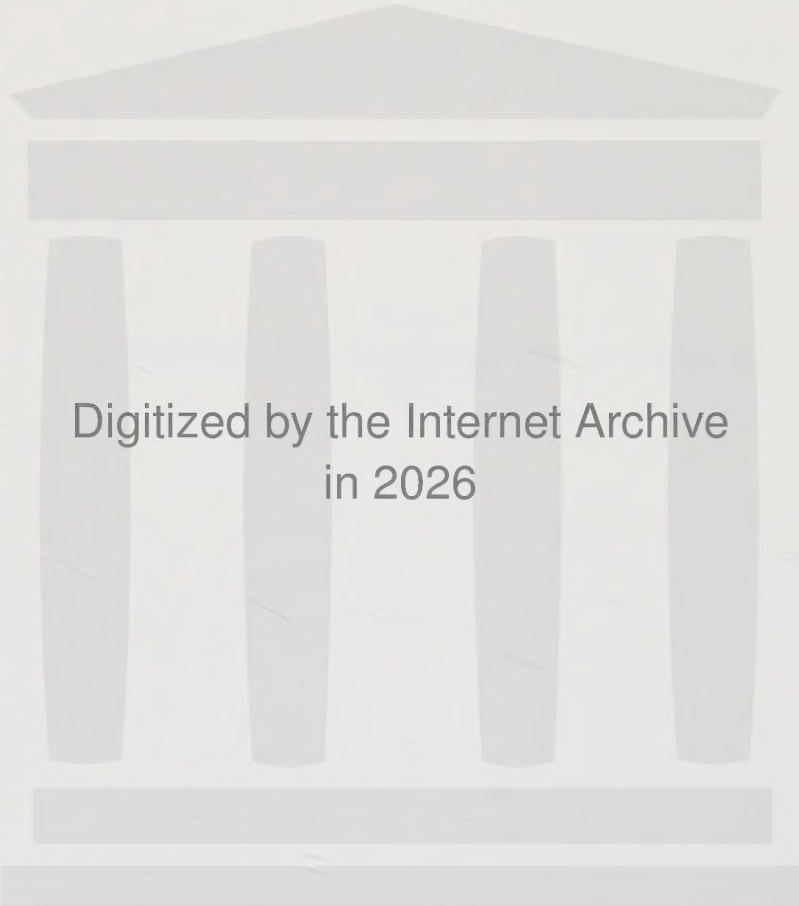
AVHANDLING FÖR TEKNOLOGIE DOKTORSEXAMEN

Avhandlingen kommer att försvaras vid offentlig disputation
å Kemicentrum, hörsal D, fredagen den 13 april 1984 kl 10.15

av

Lars Stenberg

Civ ing, Ssk



Digitized by the Internet Archive
in 2026

Direct Observations of the Real Structures of Crystals of Some Tetrahedrally Close-Packed Alloys.

**A High Resolution Electron
Microscopy Study**

Lars Stenberg



Lund 1984

Organization LUND UNIVERSITY Inorganic Chemistry 2 Chemical Center P.O.Box 740 S-220 07 Lund	Document name DOCTORAL DISSERTATION	
	Date of issue March 1984	
	CODEN: LUTKDH/(TK00-1006)/1-39/1984	
Author(s) Lars Stenberg	Sponsoring organization	

Title and subtitle

DIRECT OBSERVATIONS OF THE REAL STRUCTURES OF CRYSTALS OF SOME TETRAHEDRALLY CLOSE-PACKED ALLOYS - A High Resolution Electron Microscopy Study

Abstract

Some of the tetrahedrally close-packed alloys (σ -, μ -, M-, X-, Laves-phases and Mo_3CoSi) have been studied with High Resolution Transmission Electron Microscopy (HRTEM). Lattice images and crystal structure images reveal the existence of planar defects in a majority of the crystals. The atomic arrangement of the defects are derived utilizing intergrowth and the crystallographic operations shear, chemical twinning, slip and cyclic translations. Reasons for the existence and formation of planar defects are discussed. A short review of the discovery of the compounds, the determination of their structures, and previous electron microscopy investigations are also given.

Key words

HRTEM-studies, crystal structure imaging of alloys, defect structures of alloys, tetrahedrally close-packed alloys

Classification system and/or index terms (if any)
Supplementary bibliographical information

Language
English

ISSN and key title

ISBN
91-7222-701-X

Recipient's notes

Number of pages
89

Price

Security classification

Distribution by (name and address)

L. Stenberg, Inorganic Chemistry 2, Chemical Center, P.O.Box 740, S-220 07 Lund

I, the undersigned, being the copyright owner of the abstract of the above-mentioned dissertation, hereby grant to all reference sources permission to publish and disseminate the abstract of the above-mentioned dissertation.

Signature

Lars Stenberg

Date

1984-03-05

CONTENTS

INTRODUCTION	page 5
THE COMPOUNDS	8
THE STRUCTURES	10
PREVIOUS TEM INVESTIGATIONS	17
PRESENT TEM INVESTIGATIONS	19
<i>Experimental</i>	19
<i>The σ-phase</i>	20
<i>The μ-phase</i>	22
<i>Mo₃CoSi</i>	23
<i>The M-phase</i>	26
<i>The X-phase</i>	28
CONCLUSIONS	31
PROSPECTS	34
ACKNOWLEDGEMENTS	35
REFERENCES	36



Stenberg, L. (1984)

Thesis. Inorganic Chemistry 2

Chemical Center, University of Lund

P.O.Box 740, S-220 07 Lund, Sweden

INTRODUCTION

When short wave length electrons pass through an oriented crystal, the elastically scattered electrons (diffraction in a three-dimensional lattice) recombine in the image plane of a microscope objective lens, and the periodicity of the lattice will be imaged as contrast variations.

During the last twenty years, transmission electron microscopes (TEM) have undergone fast development with respect to resolution power. In the 1960's the resolution power of the best microscopes was in the range of 6 Å. Images taken at this time, with the so-called *lattice imaging* technique, gave fringes or patterns of unit cell multiples and revealed variations in the lattice spacings in oxides with column structures. Conclusions about the atomic arrangements in these planar defects could be indirectly derived from the knowledge of the parent structures and by the use of crystallographic operations.

Around 1970 the microscopes were capable of resolving points lying 3.5 Å apart. This enabled the microscopist to take images directly related to the real structure of crystals, if the atomic separation in the plane of projection was more than 3.5 Å. Earlier interpretations were confirmed with this further information and new compounds with column structures were studied and identified with this so-called *crystal structure imaging*. Today the resolution power is around 2 Å and a wide variety of oxides, sulfides, silicates, borates and a number of alloys have been studied with High Resolution Electron Microscopy (HREM). The reasons for doing this can be formulated as follows.

To investigate the influence of:

- constant use
- frequent regeneration
- chemical and/or physical attack

on technically important materials such as:

- solid electrolyte batteries
- electronic compounds
- catalysts
- construction materials.

Another aspect is of a more basic nature.

The full understanding of:

- the formation of different structures and defects
- the topological paths of phase transitions.

This will give us a better understanding of physical and chemical properties and perhaps make it possible to tailor-make compounds with desired properties.

Of fundamental importance for all of these tasks is an exact and general description of crystal structures, their defects and relations. This has been accomplished for many ionic compounds for a long time. Many alloys, on the other hand, initially appear to have an extreme complexity of atomic configurations and hence have not been treated until very recently. However, it turns out that the coordination polyhedra of alloys often are almost perfectly regular. The necessity of perfect polyhedra is maybe not the critical point, finding the right polyhedra is the real problem. But once it is found, many alloy structures can be treated with the same methods as the ionic ones.

One group of alloys with complex structures (and distorted polyhedra), are those with atoms in a tetrahedrally close-packed arrangement. Until recently they have resisted every attempt of complete systematization, despite the efforts of many trials. The final solution came through the methods mainly developed by Wadsley, Andersson and Hyde and applied by Andersson for the tetrahedrally close-packed alloys in his work: Structures Related to the β -Tungsten or Cr_3Si Structure Type. (J. Solid State Chem. 23, 191 (1978)). The basic thought here is that there exists a relationship between all structures, and consequently complex structures can be derived from simpler ones.

For the tetrahedrally close-packed alloys, it was shown that all of their structures could be derived from the A15 structure with crystallographic operations. From this it follows that planar defects should be present in these phases, and their atomic arrangement derived with the crystallographic operations.

The only possibility to directly study the nature of planar defects in crystal structures, and hence the validity of Andersson's ideas, is HREM. It was with this in mind that the investigation, summarized in the following pages,

was undertaken. These pages initially present a short review over the discovery of the compounds and their structures and then a summary of four published articles and some unpublished results.

The four articles cited in the following text are:

- I. Electron Microscope Studies on a Quenched Fe-Mo Alloy. Stenberg, L. and Andersson, S. J. Solid State Chem. 28, 269 (1979).
- II. Electron Microscopy Studies of Mo_3CoSi . Stenberg, L. Acta Cryst. A35, 387 (1979).
- III. Planar Defects in Crystals of Some Tetrahedrally Close-Packed Alloys. Stenberg, L. Chemica Scripta 14, 219 (1978-79).
- IV. High Resolution Electron Microscope Studies on a Quenched $(\text{Ni}_{0.5}\text{Cr}_{0.5})_7\text{Nb}_6$ Alloy. Li, D.X., Stenberg, L. and Andersson, S. J. Solid State Chem. 48, 368 (1983).

In order to facilitate studies of this work, the images and legends have been collected in a separate booklet.

THE COMPOUNDS

The first structure determination of a compound belonging to the group of alloys with tetrahedrally close-packed (tcp) structures was made on MgZn_2 in 1927 by Friauf (1). Weighted amounts of magnesium and zinc were heated under a molten mixture of sodium and potassium chlorides to a temperature 10°C above the melting point, 595°C . After slow cooling single crystals were found and Laue- and rotation photographs taken. Some months later Friauf also published the structures of MgCu_2 and CuAl_2 (2).

In 1931 a new modification of tungsten was claimed to have been prepared electrolytically by Hartmann, Ebert and Bretschneider (3). It was given the name $\beta\text{-W}$ or according to the notation of Strukturbericht, A15. Since then a great number of silicides and intermetallic compounds with this structure have been prepared and some of them are very good superconductors.

In 1935 Laves and Witte (4) determined the structure of MgNi_2 and described it as a mixture of MgZn_2 and MgCu_2 . The same year Arnfeld and Westgren (5) determined the complicated μ -phase structure (Fe_7W_6) with X-ray powder methods.

In a metallurgical survey in 1927 Bain and Griffiths (6) discovered a new hard and brittle phase in stainless steel that had been heated to around 800°C . Due to difficulties in growing crystals of suitable size and an apparently complicated structure, it was not until 1950 that Bergman and Shoemaker (7) were able to give an approximate description of the structure of a Fe-Cr (46.5 % Cr) σ -phase crystal. Some time earlier Tucker (8,9) published the structure of $\beta\text{-U}$ (containing 1.4 % Cr) which essentially has the same structure, although there still are some uncertainties about the true space-group (10). A great number of intermetallic compounds with the σ -phase structure have been prepared since then and today the number exceeds one hundred.

Systematic investigations of silicides and intermetallic compounds with related structures have in later years led to a number of new structure types that have been determined with X-ray methods. In chronological order they are:

P-phase, $\text{Mo}_{42}\text{Ni}_{40}\text{Cr}_{18}$	(11)	(12)
Zr_4Al_3	(13)	
M-phase, $\text{Nb}_{48}\text{Ni}_{39}\text{Al}_{13}$	(14)	
Mo_3CoSi	(15)	
u-phase, $\text{Mn}_{81.5}\text{Si}_{18.5}$	(16)	
X-phase, $\text{Mn}_{45}\text{Co}_{40}\text{Si}_{15}$	(17)	(18)
$(\text{Co}_{0.57}\text{Si}_{0.43})_3\text{V}_2$	(19)	
W_2FeSi	(20)	
Mg_4Zn_7	(21)	
K_7Cs_6	(22)	

The compounds mentioned here all have parallel planar atomic layers. There also exist a number of compounds with structures where the atomic layers are more or less severely rumpled. These compounds will not be treated here.

THE STRUCTURES

MgZn_2 , MgCu_2 , MgNi_2 and polytypes thereof are often referred to as Friauf-Laves phases and sometimes only Laves phases, since he was the first to systematically investigate the structures. This included discussions of atomic distances and the relation of these structures with others, MgZn_2 and MgCu_2 were compared with wurtzite and zincblende respectively, where the magnesium atoms occupied the same sites as the Zn-atoms in ZnS. Already Friauf noted that every Mg is surrounded by four others to form a tetrahedron. Both authors recognized the close relation to hexagonal and cubic close-packing. Westgren and Arnfelt saw that the Fe atoms in Fe_2W are in a nearly close-packed arrangement. However, some iron atoms are replaced by the bigger W atoms, which lie slightly off the otherwise close-packed planes. The resemblance with the more complicated μ -phase, Fe_7W_6 , was also recognized, but the fact that Fe_2W is isostructural with MgZn_2 was overlooked.

Tucker, in his work "The crystal structure of the β -phase of Uranium", describes this structure as a layer structure with two identical nets, rotated 90° with respect to each other and another net with isolated atoms sandwiched between. It was later confirmed to be isostructural with the σ -phase. In their final work on the structure of the σ -phase Bergman and Shoemaker (23) relate it to some other phases since, according to X-ray diffraction intensities, they have some general features in common.

In 1956 Kasper (24) collected data on available compounds with "new types of structure of considerable complexity", and noted that one of the general features is the occurrence of polyhedra with coordination numbers (hereafter referred to as CN) 12, 14, 15 and 16.

With spheres of equal size the best space-filling packing is achieved with the normal hexagonal and cubic close-packed arrangements. The smallest empty space created by equal spheres is however formed by four such spheres to a tetrahedron. Regular tetrahedra do not fill space, while tetrahedra together with octahedra do, as in ccp and hcp. Distorted tetrahedra can of course fill space and thus give a very efficient packing. Kasper pointed out that the coordination polyhedra with CN 12, 14, 15 and 16 all have dis-

torted tetrahedral interstices, with the central atom included, in these structures. Thus the polyhedra also have triangular, but not equilateral, faces.

If the polyhedra are constructed with spheres (atoms), it can be shown that these must differ in size in order to obtain contact. For the CN 12 (icosahedron) it is enough to insert a 10 % smaller atom in the centre. For the CN 14 the two atoms along the six-fold axis and the central one must be different in size. In the CN 15 polyhedron not all spheres can be equal, the central one must be larger than most of the atoms at the surface. The CN 15 polyhedron can be described as two 3-capped trigonal prisms sharing faces. To construct and obtain contact in the CN 16 polyhedron it is necessary to use two kinds of spheres with a radius ratio of 1.23. One larger sphere (atom) is in the centre of a truncated tetrahedron, with the four others outside the hexagonal faces created by the truncation (Friauf polyhedron). The rest can be equal spheres and are located at the vertices of the polyhedra. This gives the composition AB_2 . The formation of this kind of structure must be dependent on geometrical factors, since atoms of different sizes are involved. This approach also gives some ideas as to the ordering of different atoms at different crystallographic sites. It is natural that larger atoms occupy positions with CN 15 and 16 and the smallest atoms prefer the 12 coordination of the icosahedron. The CN 14 position is often a mixture of different atoms.

A general and exhaustive treatment of the description and classification of these structures was made by Frank and Kasper in two papers in 1958 and 1959 (25,26). In the first one they give definitions and general principles for the classification and systematization of structures with the four normal coordination polyhedra containing triangular faces. They present a formal proof that structures containing only the normal polyhedra must have planar or nearly planar layers of atoms. Half of these layers can be represented by nets containing only triangles, pentagons and hexagons. They are called primary layers and show directly the interatomic contacts within a net. Often the primary nets in one structure are identical, but rotated 90° with respect to each other. The other half of the nets are called secondary. Their vertices correspond to the positions of atoms centering adjacent polyhedra (always CN 10, 12 and 14). The atoms in one secondary net are not in contact and are sandwiched between

the atoms in the primary nets. The secondary nets are built up by squares, triangles or both and can be symbolized numerically by Schläfli symbols, see Ref (27).

The term "major ligand" is also introduced and is defined as the lines connecting two neighbouring atoms at major sites, where major sites are 14, 15 and 16 coordinated atoms. Twelve coordinated atoms are at minor sites. Two adjacent major sites must be coordinated by six atoms in common, so a major ligand is always running along a sixfold axis in the ideal polyhedron. The major ligands will then form a straight line for atoms with CN 14, subtend 120° for CN 15 and will be directed towards the corners of a tetrahedron in the case of CN 16. The major ligands build up the major skeleton, which will be a straight line, a planar net, a three-dimensional framework for CN 14, 15 and 16 respectively. In the cases of combinations of different coordination polyhedra the major skeleton may become very complicated and built by separate or connected frameworks. It is claimed by the authors that the major skeleton makes it easier to visualize and understand the structures. This is true for some structures, especially those with only one coordination polyhedron. For instance the hexagonal MgZn_2 will be reduced to only the Mg atoms and the major skeleton equal to the diamond framework. In the Al_5 structure the major skeleton will be constructed by lines connecting CN 14 atoms and running parallel to the cube axes. The name major ligand arises from the fact that it is atoms with high CN (large atoms) that are tied together.

In their next paper Frank and Kasper utilized their methods for some concrete problems. The structures of the Laves phases result from stacking triangle nets and a certain hexagon-triangle net, the so-called Kagomé-net, in different packing positions and orientations. By putting the layers in different sequences, they build up all known and some hypothetical Laves structures. From the stacking sequences it can be seen that MgZn_2 stands in a twin relationship to MgCu_2 and hence to MgNi_2 and all the other polytypes. They also derive a hypothetical structure from CaZn_5 by splitting one Ca-atom in two and thus making them 14 coordinated. In this way the CN 15 polyhedron, not present in the Laves phases, is also created. By stacking the Kagomé nets above each other and triangle and hexagon nets in between, this new structure, later to be found to exist for Zr_4Al_3 , is generated. In the stacking sequence it can be seen that the μ -phase is built up of a mixture of Laves and Zr_4Al_3 structures.

The bamboo Kagomé net is built up of hexagons sharing corners generating triangular areas in between (a 3.6.3.6 net) and is strictly hexagonal in symmetry. A modification of the Kagomé net appears when the hexagons share edges in one direction and corners in the other (a $3^2.6$ and 3.6.3.6 net). The unit cell will be rectangular with axial ratio $\sqrt{3}/2$ if ideal hexagons are used. If the net is squared the symmetry will be raised to tetragonal and the net corners describe an atomic layer in the A15 structure. The layer at $1/2 c$ will result if the first is rotated 90° and so on. Sandwiched between these are the secondary layers, which in this case will be overlapping square nets. The two variants of Kagomé nets can be mixed in an ordered way. This gives an infinite number of hexagon-triangle nets with repeating units of different shapes and sizes (Kagomé-tiling), which can be put together to form a complete representation of atomic layers. Since the squared net is involved, a distortion of the ideal hexagons is, however, always present. An example of a primary layer constructed with Kagomé tiling is found in the σ -phase structure. The secondary layer of the σ -phase structure is a square-triangle net ($3^2.4.3.4$) and the same tessellation can be used to describe the primary nets of CuAl_2 . If the squares in two such nets are placed antisymmetrically above each other, as in CuAl_2 , square anti-prisms will be created. The atoms in an ideal square anti-prism will be in a rather distorted tetrahedral packing and are perhaps better described by octahedra. However, such compounds will also be included in this treatment.

It is also possible to insert pentagons in the tessellations. With the use of symbols for different polyhedra, their orientation and environment, it is possible to designate many structures with a unique sequence. If an ordered net is interrupted by another tessellation that fits and the ordered net can continue again, it is possible to derive and describe sequence faults.

A long list of known and unknown structures are presented in the last paper by Frank and Kasper (26) and some of them have later been confirmed to exist.

Frank and Kasper's treatment, however correct in principle and far reaching, does not give the desired simple view of the structures and their relations. It is difficult to derive and visualize the atomic arrangements as expressed in symbols. The need to distort the nets gives rise to severe misfitting when sequence faults are introduced. This misfitting is enhanced with the frequency of sequence faults.

When solving the structure of the P-phase Shoemaker et al (12) recognized the importance of the four coordination polyhedra. However, they did not undertake any systematization or attempt of a general description at this point. Later, when doing so, they follow the path of Frank and Kasper, but with an improved view on the structures of the Friauf-Laves phases and the μ -phase (28). Their choices of different projection axes, still with projected planar atomic layers, give a much simpler representation of these structures. The similarity with the rest of the group of tcp's is also further enhanced in this view. They also introduce the name tetrahedrally close-packed alloys.

Their classification is based on the types of primary (main) layers and secondary layers. The structures are first separated in three different head groups depending on whether the main layers are formed by tessellations of:

1. hexagons and triangles
2. pentagons and triangles
3. alternating pentagons, hexagons and triangles

These groups are then divided into subgroups depending on the type of secondary layer.

However, this method is not singular for structures belonging to the last group unless the sequence of pentagons and hexagons is also described. For more complicated structures of this group, such as M- and P-phases, two different Schläfli notations must be given to cover the secondary nets. With further complicated examples like the X- and ν -phases, the secondary nets will turn into rather complicated formations and the point of simplifying and visualizing is completely lost.

In an attempt to give a systematical coding of the tcp's, Pearson and Shoemaker (29) have made some further modifications on Frank's and Kasper's system. Although the result is a bit simpler, it is still complicated and not valid for all the different types of tcp's, as mentioned above.

In the search for a general and exact description of crystal structures Andersson and different co-writers have published a number of articles (30, 31,32). Their arguments and tools emerge basically from those of David Wadsley,

who was the pioneer of the concept of extended defects and building blocks in structure description.

The essence of the current status of these ideas has been published recently by Andersson (33) and the ultimate criteria are formulated as follows:

A structure description shall:

1. be simple and show as many relationships as possible to other structures,
2. facilitate the explanation of diffusion and reaction mechanisms,
3. be useful in explaining physical properties like conductivity, hardness etc,
4. be helpful to interpret high-resolution electron microscopy lattice images - this often means trying to understand the defect structure of a crystal.

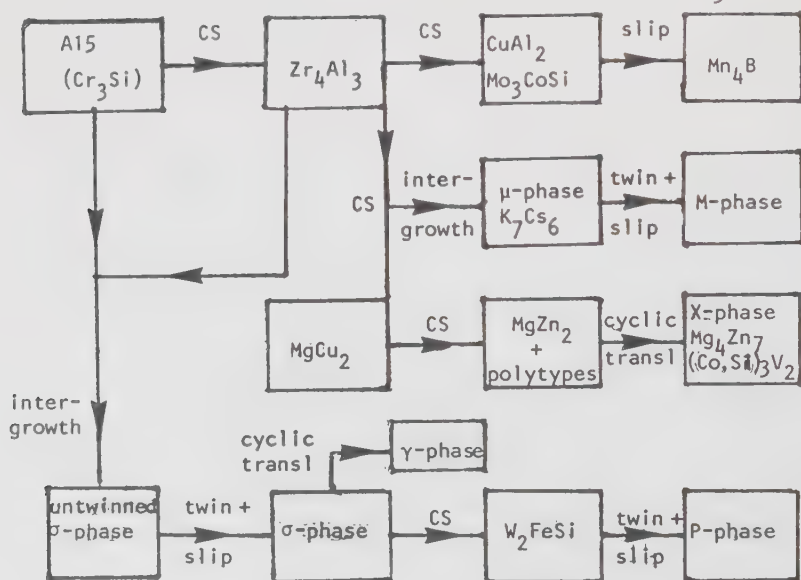
Underlying these statements are of course the demands of exactness and validity for compounds with metallic, covalent and ionic character.

In line with the basic principle of simplicity the simplest possible polyhedra should be used. It is enough, in most cases, to use only the tetrahedron, cube, octahedron and trigonal prism. Other, bigger, polyhedra occurring in complicated structures can be constructed or generated by these, simultaneously giving a more accurate description. The polyhedra mentioned here can, separately or mixed, build up larger units that may or may not be identical. These parts can repeat in one, two or three dimensions to complete a final structure providing they fit together. The repetition obeys the crystallographic laws, but the similar operations are called: crystallographic shear (CS) (translation), slip (glide), chemical twinning (reflection) sometimes combined with slip and cyclic translation. When two different parts, or blocks, are put together we talk about intergrowth.

It is interesting that, in this approach, extended (or planar) defects must be related to the building-blocks and can be derived from them.

In the case of the tcp's, the tetrahedron itself is the basic element in their description. Five empty and irregular tetrahedra can be used to build up what Schubert calls a Tetraederstern (hereafter referred to as TS) (Fig 1a) and it is sometimes easier to put emphasis on this constellation instead of the tetrahedra themselves. This was used by Andersson (34) in the paper dealing with "Structures Related to the β -Tungsten or Cr_3Si Structure Type". In this article a number of tcp's are derived with the use of the crystallographic methods mentioned above, from the A15 structure (β -W, Cr_3Si). Later (35) cyclic reflection and cyclic intergrowth have been included to give a better picture of some of the structures.

The A15 structure, projected along a cube axis, can be described using only TS's sharing corners (Fig 1b) and the atoms centering the hexagonal antiprisms created by the TS's. If a CS operation is carried out in $\{100\}$, with a displacement vector $\frac{1}{4}[010]$ in a regular way, the resulting structure is the ideal structure of Zr_4Al_3 along $[110]$ (Fig 2). If this atomic arrangement is projected along its hexagonal c-axes, it can be described with trigonal bipyramids alone, sharing corners (Fig 3). The hexagonal anti-prisms thus generated are filled with atoms at $1/4$ and $3/4$, sandwiched between the atoms at 0 and $1/2$. Regular CS-operations can also be performed on this structure along $\{120\}$ resulting in the MgCu_2 structure (Fig 4). Various chemical twinning on this structure gives MgZn_2 , MgNi_2 and all the other polytypes. Different intergrowth combinations with Cr_3Si - and MgCu_2 -structures can be used together with the other crystallographic operations, to derive all possible structures of the tcp alloys. Below the relationships of all known structures to Cr_3Si are demonstrated.



PREVIOUS TEM INVESTIGATIONS

The appearance of σ -phase particles in stainless steel, sometimes giving a material fatal properties, has attracted a great deal of technological attention during the years after its discovery by Bain in 1927 (6). After the structure determination of the σ -phase structure was carried out independently by Bergman and Shoemaker (23), Dickins, Douglas and Taylor (36) and by Kasper, Decker and Belanger (37) and by Tucker for the β -U structure (9) in 1951, a great number of theoretical studies have been done. Some of these papers concern structure determining factors, transformation paths from bcc to σ -phase and, as mentioned earlier, structure properties and relations.

In 1952 Holden (38) showed, to great surprise, that single crystals of β -U were ductile with slip in the $\{110\}$ planes. Polycrystalline β -U samples were known to have a certain degree of brittleness and the σ -phase crystals always to be very brittle. Since slip in ductile materials is known to be associated with dislocations in the slip directions, it was considered to be of great interest to see if the brittle σ -phase also contained these. If not, the ordering of atoms present in σ -phase crystals, should be responsible for the absence of dislocations and hence for the brittleness. With this in mind, and also the suggestion by Frank and Kasper of possible sequence faults, Marcinkowski and Miller undertook a transmission electron microscopy survey of the Fe-Cr σ -phase (39). Their samples were heat treated prior to electrolytic thinning and studied in a 100 kV TEM without facilities to orient their crystals. With the use of brightfield and darkfield imaging modes, Marcinkowski and Miller were able to give nice proofs of the presence of planar defects. Since orientation of the crystals was not possible and high resolution not obtainable, a very small objective aperture was used, in order to ensure high contrast and to avoid unwanted diffracted beams contributing to the image. Fringecontrast variations can be observed in a faulted area if different single diffraction points are allowed to pass through the aperture, since the phase angle of diffracted electrons change during passage through a faulted region of a crystal. It is possible to calculate the phase-angle for a probable fault vector and a reciprocal lattice vector. By using this, the expected contrast variations in the fault can be estimated. By observing the contrast variations over a faulted region, with the contribution of single diffraction points to the image, the validity of a fault vector can be confirmed. By doing so they were able to show that the faults run

along the $\{100\}$ and $\{010\}$ planes and presumably were of the Frank and Kasper type. Sometimes these faults crossed each other, but no explanation was given for the atomic arrangements in the cross-over. Faults lying in non-crystallographic planes and defects forming loops were also frequently observed, but were not analysed in detail. The complete absence of glissile dislocations associated with slip, give good evidence for the proposal that ordering of atoms of different sizes prevent the formation of this type of dislocations. Parts of the α -phase, in incompletely transformed grains, were however often found to be heavily disturbed by dislocations, while the other side of the α - σ boundary was free from them. Planar defects in the σ -part seemed to start at the boundary and run perpendicular to it as they had been introduced by the phase transition, indicating a long range ordering in the bcc α -phase.

The first lattice fringe imaging, of compounds with tcp structures, was done by Allen et al (40) on TiCr_2 and TiCo_2 with Laves phase structures. They were able to image stacking faults in electrolytically thinned crystals and to determine three new stacking variants in these systems.

In 1977 Kitano et al (41) published a study with lattice fringe imaging of Laves phase crystals in the Mg-Cu-Al system. They also showed evidence of stacking faults and were able to identify some new stacking variants from the images and their diffraction patterns. However, no crystal structure imaging was obtained since the a-axis of the hexagonal cell was chosen as the projection axis and the resolution was slightly too low. The interesting observation of an increased number of stacking faults in rapidly cooled materials, as compared to tempered ones from the same bulk sample, was also made.

Later work by Kitano et al (42) with higher resolution and $[110]$ as projection axis, gives crystal structure images of Laves phase polytypes and their stacking sequences. These can be directly determined from the images. All images taken by Kitano et al were from electrolytically thinned crystals.

PRESENT TEM INVESTIGATIONS

Experimental

The methods of describing crystal structures developed mainly by Wadsley, Andersson and Hyde for ionic compounds (43,44) and later extended by Andersson to include alloy structures are superior to all other descriptions in the interpretation of crystal structure images and defects in crystals. Furthermore Andersson's description (34) unites the structure building principles of ionic, covalent and metallic compounds. These methods will be used in the following.

Curiously enough no one seems to have taken advantage of the most spectacular property of the tcp's, their brittleness. In the present investigation systematic use of this property has been applied to the study of all these alloys. All samples have been crushed in an agate mortar, just as ordinary oxides. This technique is superior to every other, since there is no chemical attack on the material, as might happen with chemical etching or ion-beam thinning. An extremely easy sample preparation is also provided by this procedure.

The TEM investigations have been carried out in two different microscopes. One is a Philips EM 400, equipped with a side entry goniometer, always operated at the maximum voltage of 120 kV. The spherical aberration coefficient C_s is 2.5 mm and the halfwidth of the defocus spread distribution, due to high voltage and lens instabilities, is approximately 100 Å. The beam divergence was calculated to be $7 \cdot 10^{-4}$ rad. The sample holder allows 360° rotation and a tilt of $\pm 20^\circ$.

The other microscope used was a JEOL 200CX equipped with a top entry goniometer stage with $\pm 10^\circ$ double tilt sample holder, which gives superior stability and enables long exposure times. The corresponding microscope constants are: $C_s = 1.2$ mm, halfwidth of defocus spread is 30 Å, the beam divergence is $6 \cdot 10^{-4}$ rad and acceleration voltage 200 kV.

The optimal resolution is roughly given by the expression $D = 0.63 \cdot C_s^{1/4} \cdot \lambda^{3/4}$, which gives resolution capabilities of 3.5 Å and 2.2 Å in crystal structure imaging. Slightly higher values are reached in practice, since the chromatic aberration and the beam divergence have a damping effect on the contrast

difference at the resolution limit. A further advantage with high accelerating voltage is the increased penetration of the electrons, which is of great help, especially in the study of alloys and other compounds where absorption is severe.

The sample, sometimes crushed in liquid nitrogen, was suspended in methanol and transferred to a copper grid coated with a holey carbon film and locked to the sample holder. The crystals were always oriented to the desired projection in diffraction mode, with the help of the Ewald sphere, to ensure an optimal alignment. Crystals with sharp edges were in general rather easy to find and align, but very often turned out to be too thick. Parts thin enough to give phase contrast were eventually found, but usually only in a rather narrow region of the crystal.

The σ -phase

Because of its high technological interest and fame, the σ -phase was the first object to be studied (1). A fifty-fifty mixture of Fe-Mo was compressed to a pellet and melted in an argon arc furnace. The product gave an X-ray powder diffraction pattern with some very diffuse and broad lines, but the presence of the σ -phase could be confirmed. Crystallites giving the characteristic electron diffraction pattern of the σ -phase were fairly easy to obtain, but although a substantial number were imaged, no traces of planar defects or dislocations were seen. A typical example of a lattice image with the beam parallel to the c -axis is shown in Fig 5a. A theoretical image produced with the multislice method was made with a program by P. Fejes and I. Skarnulis. The ordering of atoms and parameters given by Wilson and Spooner (45) were used in the calculations, which gave a pattern of white dots as can be seen in Fig 5b. The program also chose the correct unit cell and from this it could easily be seen that the positions of the white dots corresponded to the encircled areas in Fig 5c. According to Wilson and Spooner the four atoms encircled are Mo. In the calculations an underfocus of 900 Å and six slices ($c = 4.81$ Å) were used.

Other compositions with Mn-Cr and more extensively a number of Fe-Cr σ -phase alloys, with varying degree of Si, Ni and Mo, have also been investigated (111). The Fe-Cr samples were kindly provided by Sandvik AB and had been prepared by slow cooling from the melt (1200-1500 °C) and tempered at 850 °C for 48 h.

The best images were always recorded from the pure Fe-Cr alloy, where distinct white dots appeared in zig-zag rows (Fig 5d). The positions of the white dots were in this case presumed to correspond to the positions of the atoms in the hexagonal anti-prisms (double circles in Fig 5c). Later work by Ishimasa et al (46,47,48,49), O'Keefe et al (50) and Southwick et al (51) have fully confirmed this interpretation with images and calculations.

The existence of planar defects of the type predicted by Frank and Kasper and first showed by Marcinkowski and Miller are also fully confirmed by these authors. The structure of this type of defect can, according to Andersson's terminology, be derived by a chemical twin operation followed by a slip. This operation was used by Andersson in the derivation of the σ -phase structure from a hypothetical structure, which in turn was derived from the A15 structure.

Ishimasa also gives a detailed explanation of the atomic arrangement in the crossover of defects, first observed by Marcinkowski and Miller. It turns out that two possibilities occur, but are easily distinguished in a high resolution micrograph. One of them forms a six-ring of white dots around a central one and corresponds to a piece with Zr_4Al_3 structure, viewed along the c-axis. The other one forms the A15 structure in the crossover and this will turn up as a square of nine (3x3) white dots in the micrograph. Another very interesting defect, explained by Ishimasa, runs along {110} and the atomic arrangement is described as alternating pieces of a TS and six trigonal bipyramids connected as in the Zr_4Al_3 structure. There seems to be no perfect fit when {100} and {110} defects meet and they never seem to cross each other. Instead they are forced to form closed loops, which was also reported by Marcinkowski and Miller. The surroundings of defect intersections, with atomic arrangements which for some reason do not fit together, always seem to contain defects not lying on crystallographic planes. Ishimasa gives models for these defect areas, but the interpretation must be considered uncertain since the quality of the strained areas is poor, as a result of the nature of the defects.

Neither Southwick et al nor Ishimasa et al have recorded any presence of dislocations. Both studies were performed on electrolytically thinned samples, although the former also have studied crushed material, but report that defects are rarely seen. No image of a defect in crushed material has been published.

The μ -phase

Another phase, not identified in the X-ray diffraction powder pattern, was found in the Fe-Mo sample and shown by electron diffraction to be the μ -phase (Fe_7W_6) (1). The structure of the μ -phase is described by Andersson as an intergrowth of one slab with Zr_4Al_3 structure (along $\{110\}$) and one with MgCu_2 or MgZn_2 structure (Fig 6a). In contrast to the σ -phase, μ -phase crystals frequently contained a great number of defects of various kinds. This could already be seen in the electron diffraction pattern, which showed streaking in one direction (Fig 6b). Crystal structure imaging was not obtained for the Fe-Mo μ -phase crystals. Lattice fringe images, sometimes split up to give unit cell resolution, were however easily obtained and showed clear evidence of three different kinds of defects. In Fig 6c, which is an electron micrograph of a Fe-Mo μ -phase crystal with unit cell resolution, an irregular wavy structure can be seen, especially at an inclined angle. This change of direction of the projected unit cell is achieved by one twin operation in a plane where the Zr_4Al_3 - and MgCu_2 -parts join, as described in Fig 6d. If this operation is carried out in a regular way, one possibility will result in the structure of K_7Cs_6 described by Simon et al (22). In this case no change of coordination polyhedra will occur in the twin plane.

The presence of the twin defect was later (IV) fully confirmed with crystal structure images in crystals from a Ni-Cr-Nb alloy. In Fig 7a the atoms centering the pentagonal anti-prisms (double circles in Fig 6a) correspond to the white contrast in the micrograph. This was also confirmed with calculated images, as can be seen in the lower right corner of Fig 7a. The micrograph in Fig 7b is also from a Nb-Ni-Cr μ -phase crystal and it is easily seen from the pattern of the white dots, that in one part it is different from Fig 7a. Instead it is here identical with the K_7Cs_6 structure as seen in the inserted drawing.

Since the μ -phase structure is composed of slabs of two different structures, it was presumed to contain intergrowth defects. A μ -phase crystal, from a Mo-Co-Si sample, is shown in Fig 7c (III). It is clearly seen, at the arrows, that $3 \times \infty$ white dots (pentagonal antiprisms) instead of $2 \times \infty$ are present in the defect. This will be the result if one extra sheet with the Zr_4Al_3 structure is allowed to intergrow in the μ -phase structure. The atomic ar-

rangement is given in Fig 7d. This type of defect was also suggested to explain a crystal defect from the Fe-Mo sample (Fig 7e). Since the resolution was poor, no separation between an intergrowth of Zr_4Al_3 - and $MgZn_2$ -structures could be done. With sufficient resolution, the distinction between the two types of defects is quite clear (Fig 7f). The third type of intergrowth that can occur in μ -phase crystals is that with $MgCu_2$ structure type (Fig 7g). Evidence of this defect can be seen in Fig 7h. However, the spacing over the defect is doubled, which can be explained by an ordering of atoms. The Mo atoms must occupy the CN16 positions, but since the preparation composition was 50/50 Fe-Mo, it is likely that the μ -phase crystals in this case have an excess of Mo. The true Laves composition should be $MoFe_2$ and it is believed that extra Mo atoms also occupy CN12 positions, and do so in an ordered way, hence doubling the lattice spacing (Fig 7i).

The Ni-Cr-Nb sample mentioned above also contained crystals with the $MgZn_2$ structure and an example of this is given in the micrograph of Fig 8a, where the structure drawing and calculated image are inserted. Also here the white dots represent the positions of the atoms in the pentagonal anti-prisms, as has already been assumed for the defect shown in Fig 7f. Crystals with the $MgZn_2$ -structure often contained defects with the μ -phase structure (Fig 8b) and sometimes with the twinned μ -phase or K_7Cs_6 structure (Fig 8c).

Mo₃CoSi

If the A15 structure is looked upon as an analogue of the ReO_3 structure, with an infinite array of TS's instead of octahedra as in ReO_3 , it can be used to derive new structure types with the crystallographic shear operation, which has been done so successfully for the niobium oxides (30,52). The CS operation is defined as a cooperative translation of blocks or columns of atoms, with the resulting shear vector always at an angle to the resulting shear plane. If the shear vector points towards the shear plane an omission of atoms will always occur. In the case of the niobium oxides this will also result in an increase of CN for the atoms in the shear plane, while the opposite will occur for some atoms in the tcp's, causing a lower average CN. The terms positive crystallographic shear (PCS) and negative crystallographic shear (NCS) was hence introduced to distinguish between cases where the resulting shear vector points towards or away from the shear plane respectively (11).

If PCS is carried out in the A15 structure so that the TS's share edges in one direction it will result in an idealized version of the Zr_4Al_3 structure. Similarly, if the operations are carried out in perpendicular planes it results in the $CuAl_2$ or Fe_2B structure. It is clear from this description that a great number of possible structures exist between the A15 and $CuAl_2$ structures. By analogy with the oxides, the A15 structure is the $\infty \times \infty$ (corresponding to ReO_3) structure, Zr_4Al_3 is the $1 \times \infty$ block structure and $CuAl_2$ the 1×1 column structure. The only other structure built only with TS's is the 2×2 column structure of Mo_3CoSi . The average coordination number (ACN) for these structures are:

A15	13.5
Zr_4Al_3 , Mo_3CoSi	13.43
$CuAl_2$	13.33

In order to study whether Wadsley- or shear-defects are present in the real structure of crystals of Mo_3CoSi , it was prepared from the elements in a solid state reaction in sealed quartz tubes (11). In the microscope the crystals were aligned so the short c-axis was parallel to the electron beam. A structural drawing of this projection is given in Fig 9a, where the TS's with heavier lines show a 2×2 block. Crystals that could be aligned along the desired axis were easily found, but often turned out to be too thick to give crystal structure images. Sometimes it was possible to find and orient small crystals growing out from a bigger particle and these were often much thinner and gave better resolution. An example of this is given in Fig 9b, where a number of planar defects are also visible. The interpretation of the image, confirmed by calculations (Fig 9c), shows that the stronger white dots correspond to the position of the atoms in the hexagonal anti-prisms. The weaker greyish spots appear at the positions of the atoms centering the square anti-prisms. From this it can be deduced that the planar defects arise from a type of Wadsley defect, where hexagonal anti-prisms become neighbours, (Fig 9d). The local atomic arrangement in the defect can be derived with a NCS operation, with the shear vector perpendicular to the shear plane. The ACN will be increased by this operation. In Fig 9e an ordered arrangement of three NCS defects run parallel and in Fig 9f the structural drawing of this 2×3 column structure is given.

It is possible for two NCS defects to cross each other without introducing any strain in the crossover. An example of this is also seen in Fig 9b, where the four white dots in the crossover are clearly seen. The structure of this defect is given in Fig 9g and it can be seen that a piece with the Al_5 -structure, which we used to derive the Mo_3CoSi structure with, is formed in the crossover.

Another type of defect, frequently encountered in crystals of Mo_3CoSi , introduces a shift of the atoms on different sides of the defect (Fig 10a) (111). From the crystal structure image the slip vector appears to be $\frac{1}{8} \langle 110 \rangle$. From geometrical considerations of the structure a shift of $\frac{1}{4} c$ must also be present to keep interatomic distances at a reasonable length. Furthermore, it is likely that the atoms at the defect plane take the positions of the atoms in the former antiprisms. If the defect lies in $\{110\}$ -planes, a small translation away from the defect plane must take place (Fig 10b), but in the case of similar defects in $\{220\}$ -planes, a pure slip operation can be used to derive the defect. The exact structure of the defect area can not be deduced from the image in Fig 10a, but if an otherwise perfect structure is assumed, the image shows a $\{110\}$ -defect. If a pure slip operation is carried out between the slabs of TS's in Zr_4Al_3 as described above, it will result in the structure of Mn_4B with all B atoms present (53) (Fig 10c). The coordination polyhedra across the defect area will, in the case of Fig 10c, be the same for CN15 and CN16 as for the tcp's. The atoms at the unshared corners of the TS's acquire a CN of 10 and 11, but here the coordination polyhedra become non-regular and very complicated, with not only tetrahedral interstices. Mn_2B has the CuAl_2 structure, which can also be used to derive the Mn_4B structure by parallel slip operations, as described above for the $\{110\}$ defect.

Defects of slip type running parallel to the crystallographic a -axis, of the tetragonal Mo_3CoSi , were sometimes observed. They always connected planar defects of various types (Fig 11a). A suggestion of a possible arrangement for the atoms in the defect, that fit with the image, is given in Fig 11b. The atomic positions can in this case not be derived directly with a slip operation. A similar arrangement is found in the structure of $\eta\text{-Pu}_{19}\text{Os}$ (54) although the atoms in this case form rather distorted TS's. The atomic fit along the defects is indeed not perfect, as can be seen near the defects at an inclined angle, and their length seems to be rather short. As mentioned above, these defects connect other planar defects, thus making it possible

for them to form loops and hence terminating the progress of them. If it is assumed that the planar defects are formed in the crystallization process for chemical reasons (for example non-stoichiometry), the defect must continue because of its geometrical nature even if this chemical reason expired. The alternative, which is to terminate a planar defect, inevitably introduces high strain with local disorder. This has also been observed by Ishimasa in σ -phase crystals (48). It is however quite obvious that Nature prefers to form loops in crystals of Mo_3CoSi and may do so with the use of slip defects that do not necessarily have a perfect geometrical fit. This is probably also the case in σ -phase crystals, where Marcinkowski and Miller (39) and Ishimasa (49) have imaged closed loops, since there exist some possible arrangements for slip in the $\{110\}$ -planes in the σ -phase structure.

The dark planar defects of the Wadsley type present in Fig 11a can be derived from the Mo_3CoSi structure with PCS operations. The resulting structural drawing is given in Fig 11c and in case defects cross each other a piece of the CuAl_2 structure will form.

The M-phase

The M-phase structure can be derived from the μ -phase structure with regular twin operations, followed by glide operations (slip), see Fig 12a. The resulting structure contains all of the four normal Frank-Kasper polyhedra, but is easier visualized with TS's and trigonal bipyramids, as shown in Fig 12b where the μ -phase structural parts are indicated. With a sufficiently powerful microscope, M-phase crystals give white contrast from the atoms in the pentagonal anti-prisms, shown with double circles in Fig 12b. A good example of a crystal structure image of an M-phase crystal is given in Fig 12c, where the regularity of the string of white dots is interrupted at one place. This arrangement is easily explained with a twin and a slip operation along the defect plane, producing a larger part with the μ -phase structure (Fig 12d). Crystals of the M-phase often contain a wide range of sizes of μ -phase regions, but are frequently too thick to give good images. A nice image of an extreme example is given in Fig 12e, where large parts with the μ -phase structure are linked together as in the M-phase. Further inside the crystal the M-phase structure is predominant, which can also be deduced from the electron diffraction pattern of Fig 12f taken from another part of the actual crystal. Fig 12g shows the electron diffraction pattern over the defect area,

where the diffraction spots are elongated in one direction. Note also the similarity of the electron diffraction pattern of Fig 12g to that of a μ -phase crystal in Fig 6b.

Another example of an M-phase crystal is given in Fig 12h, where two cracks cut the crystal in the projection direction, with the normal interatomic bonds broken. Just to the left of these cracks is an area with severe strain in the structure. According to the image the structure seems to be a bit bent and hence must have some degree of ductility. This effect has also been noted for all the other tcp compounds, since the electron diffraction pattern very often has different orientations from different parts of the crystals. The deformations of the crystal in Fig 12h must have been introduced in the grinding of the sample, since the defects in the structure have the same width on each side of the faults. It is also interesting to see how drastically the contrast changes in Fig 12h, due to focus and alignment variations.

The part with the M-phase structure in Fig 12h is a piece of a bigger particle with a much simpler structure, which can be seen to the right in the figure. Closer inspection of this part reveals two sets of lattice fringes with approximate spacings of 3.3 Å and 6.4 Å and 48° apart. The fringes with 3.3 Å spacing form an angle of 6° with the a-axis of the M-phase structure. It is clear from this image that the defects are introduced in the M-phase in the transformation process from something that is probably an ordered bcc structure, as was shown by Marcinkowski and Miller for the σ -phase. The exact ordering of atoms in the bcc phase is of course impossible to determine from this image, since the differences in the atomic sizes are too small. However, it should be possible to derive a topological transformation path from the imaged fringe spacings and angles. Slightly better resolution and exact electron diffraction patterns would be of great help and may be of fundamental importance in solving this problem completely.

It has been mentioned earlier that a planar defect once formed, must continue by geometrical (size-factor) reasons. The defect may thus have to progress, without any chemical motivation to do so, by forcing the elements present to occupy atomic positions geometrically created for others. This must introduce strain at the phase boundary where a defect starts, that may attract elements of a more suitable size from the bcc phase, in order to release some of the strain. The alternatives are to terminate the defect, thus causing heavily

distorted areas with concentrated high strain, or to form loops with the help of slip defects where this is possible.

The X-phase

The structure of the X-phase ($\text{Mn}_{45}\text{Co}_{40}\text{Si}_{15}$) was determined by Manor, Shoemaker and Shoemaker (17). Although it contains all the normal coordination polyhedra, it could not be described with the methods developed by Frank and Kasper and Pearson and Shoemaker. Andersson (in Ref (34) it is wrongly called X-phase), identified pieces in the X-phase structure with the MgZn_2 -structure, that could be translated by fourfold rotation, combined with reflection, to give a closed unit. If this unit is filled with additional atoms to form a TS in the rotation centre, it can be used to build the entire structure by repetition in three dimensions, see Fig 13a.

Another way of deriving the X-phase structure and other similar ones, has later been demonstrated by Andersson (31). If two identical parts with MgZn_2 -structure are put together as in Fig 13b, it results in perfect fit except for the centre, where two pairs of atoms come very close together. These atoms are 12-coordinated in the Laves structure, but if they are substituted by two bigger ones they can form a TS, see Fig 13b, where they are 14-coordinated (two CN 16 go to CN 15 as well). Parts with the Laves structure can then be added and the operations described above repeated at different intervals in a regular way in the two directions. Starting with the MgZn_2 structure a long range of structures can be derived and, since CN 14 positions are introduced, the general formula must be $\text{Mg}_{1+x}\text{Zn}_2$. One member of this series has been found to be Mg_4Zn_7 (see Fig 13c). One other structure of this type, but with different composition, is known. With shortest possible distances between the TS's it is identical with the structure of $(\text{Co}_{0.57}\text{Si}_{0.43})_3\text{V}_2$ (Fig 13d).

A hypothetical example with extended Laves parts in one direction is given in Fig 13e and the calculated composition in this case should be $\text{Mg}_{45}\text{Zn}_{55}$. If twin operations are carried out along the heavy lines in Fig 13e it will result in the X-phase (composition $\text{Mn}_{45}(\text{Co},\text{Si})_{55}$). That the hypothetical structure of Fig 13e is a possible arrangement was clearly seen in the frequency of planar defects with this structure in the crystals of X-phase. An example of this can be seen in Fig 13f, where the defects run parallel to the

y-axis. The white dots were found by computer calculations to come from the positions of the atoms in pentagonal anti-prisms (Fig 13g) shown by bigger dots in Fig 13a. This atomic position contains 42.5% silicon according to the structure determination (atomic pos. 3 in Ref 17), while the adjacent position (atomic pos. 2 in Ref 17) contains no Si. If the defects of Fig 13f were a result of different ordering of atoms, the pattern in the micrograph would look different than it does. If however a twin operation of the type previously described, and the system of ordering is kept, a good agreement with Fig 13e is achieved. The bigger circles indicate the positions of the atoms giving white contrast.

It is also possible to carry out a twin operation along the x-axis and the result is given in Fig 13h, where the positions of the white dots are also indicated as described above. In Fig 13i a crystal of the X-phase with three such defects is shown (see arrows).

As can be expected from the different methods of derivation of the X-phase structure, the variation of possible planar defects is great. Apart from the two types already discussed, the X-phase structure apparently has the possibility of planar defects along (110) planes. This has been recorded for a number of crystals together with other faults, not lying on crystallographic planes. A more detailed analysis of this has been undertaken in cooperation with David J. Smith of the High Voltage High Resolution Group in Cambridge and will be published elsewhere.

Very brief investigations have been done for some other tcp's such as Mg_4Zn_7 , the P-phase, the ν -phase and V_3Si with the Al5 structure.

The first two compounds frequently contain planar defects of the types described above. Mg_4Zn_7 is however not as brittle as the other compounds studied here. Because of this it is extremely difficult to align properly. Different sizes of the MgZn_2 -parts in this structure are clearly visible, although the micrographs are of poor quality.

Crystals of the P-phase were fairly easy to find and align, but inevitably turned out to be too thick to enable good images, even at 200 kV.

Crystals of the ν -phase that were possible to align have only been found

twice. Some structural features of the projected cell can be seen in the best micrograph, but show no sign of any defects. In the other a defect, probably planar, can be seen near the edge of the crystal.

Quite a number of crystals of V_3Si with A15 structure have been studied. No sign of planar defects was recorded.

CONCLUSIONS

There is no doubt that crystal structure imaging is a superior method to reveal the local atomic arrangements in the actual structures of crystals of tetrahedrally close packed alloys.

The interpenetrations of the crystal structure images are simplified by the use of the structure descriptions of Shoemaker and Shoemaker (28) and Andersson (34). However, an understanding of the structure of the planar defects, frequently encountered in crystals of these compounds, is best achieved through Andersson's methods. The basic idea here is that all structures of the tcp alloys can be derived from the simple A15-structure, with crystallographic operations which are invariant. This includes the fact that the nature of the planar defects is inherent in the structure in which they exist. Further advantages with Andersson's method are its generality: it is valid for ionic as well as covalent and metallic compounds and generates exact positions.

It has been demonstrated here that high resolution electron micrographs, showing structural features of crystals of tcp alloys, can be easily and accurately explained and described by the use of the methods and criteria given above.

Guidance in the search for new structure types is achieved by observation of planar defects, especially if they occur in an ordered way. Together with the knowledge of the ordering of atoms at specific sites, determined by size and electronic structure, proper compositions can be calculated for syntheses. It is our firm belief that new structure types, belonging to this group of compounds, can be prepared if proper conditions and methods of syntheses can be found.

The transformation process from a bcc structure to the tcp is very sluggish, but can be made faster by plastic deformation or heat treatment prior to the transformation. Because of this it has been proposed by several authors (see Ref 55), that an ordering of atoms and vacancies will take place before the transformation. It has been shown by Marcinkowski and Miller and in this work, that the planar defects must be formed in the transformation process, since they have been seen to start in the phase-boundary between the bcc and tcp parts of crystals and to grow perpendicular to this boundary. If geometrical

factors are important in the formation of a specific coordination polyhedron, it must be logical to assume that the presence of planar defects is a way for Nature to accommodate changes in stoichiometry. Since a planar defect cannot terminate itself without causing high local strain, it is likely that the planar defect acts as a source of attraction for impurities and atoms deviating from stoichiometry in its attempt to progress. When foreign atoms are no longer available, Nature seems to prefer the formation of closed loops when this is structurally possible. The alternative, which is simply to stop, seems to be avoided.

Further studies of partially transformed crystals, with crystal structure imaging and electron diffraction will probably yield the key to understanding how the atoms are ordered. Since an apparently simple tcp structure may demand a very sophisticated preordering, hence requiring a not easily obtainable long range order in the bcc state, a complete solution of this problem will give us the answer as to why certain structures are preferred.

Most investigations by others in this field have been carried out on samples prepared by solid state transformations. Here all but one sample (Mo_3CoSi) have been prepared from the melt. This was done in an argon arc-furnace with the samples resting on a water-cooled copper plate. Despite this rapid cooling, crystals of the tcp alloys were formed. Two possible conclusions can be drawn from this fact:

There is a certain degree of ordering - at least over a short range - already in the melt.

The ordering process is rapid and the transformation is sluggish.

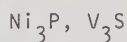
The last conclusion is, at least to some extent, supported by the observations of partially transformed crystals. Despite this fact, intuition suggests that the first alternative is more likely, but that the rate of transformation is not negligible. No quantitative analysis of the fraction of transformed crystals can be done, since the brittle crystals are enriched in the grinding and preparation process.

If a certain degree of ordering does exist and the transformation process is

not instantaneous, it is natural to expect that a rapidly quenched sample would contain a mixture of bcc- and TS-units and maybe trigonal bi-pyramids. It is then interesting to observe that the structure of Ni_{12}P_5 can be described as a cyclic intergrowth of solely TS- and bcc-units (35). Ni_3P is built by separate TS's only and, together with Ni_{12}P_5 , it is known to easily become amorphous. One kind of glassy or amorphous metal often has compositions of approximately 80% metal and 20% of a metalloid like B, C, Si, P. It is interesting to look at the compositions of some tcp alloys with this in mind.

Mo_3CoSi	$(\text{Mo}, \text{Co})_4\text{Si}$
v-phase	$\text{Mn}_{81.5}\text{Si}_{18.5}$
$(\text{Co}_{0.57}\text{Si}_{0.43})_3\text{V}_2$	$(\text{Co}, \text{V})_{2.85}\text{Si}$
X-phase	$(\text{Mn}, \text{Co})_{85}\text{Si}_{15}$
W_2FeSi	$(\text{W}, \text{Fe})_3\text{Si}$

Some other compounds built with TS's give:



An infinite number of combinations of TS's - and bcc-units exist to form structures and give a simple explanation for the structure of amorphous alloys. Many of these structures can in their turn intergrow, both in a cyclic and parallel way. Particles with structures, that can be explained in this way, have indeed been found in a sample with bulk composition $\text{Mn}_{80}\text{Si}_{20}$ (56).

PROSPECTS

The next generation of high resolution transmission electron microscopes will be commercially available in the very near future. They will be operated at an accelerating voltage of 350-400 kV and will give an approximate resolution of 2 Å in crystal structure images. This will give information at a finer scale and provide better transmission of the electrons. This will make it possible to include those tcp alloys with heavy electron absorption for the kind of studies described in this text.

Video recording of images from the microscope, combined with a heating holder for the sample, should make it possible to record the dynamic processes of phase-transitions from the bcc- to the tcp-phases in partly transformed particles. This should explain the behaviour of defects, especially those which link together other planar defects to form loops, and of course also give a better understanding of the phase-transition itself.

Chemical analysis of extremely small particles by the use of electron microscopes, with the techniques of Energy Dispersive Spectroscopy (EDS) of X-rays and Electron Energy Loss Spectroscopy (EELS) has developed rapidly during the last few years. This combined with the smaller size of the electron beams (~ 30 Å), which follow from new lens designs and materials, will make it possible to analyze over a defect area. Eventually deviations from stoichiometry and the detection of small amounts of impurities can be accomplished with these methods and related to the nature of the defects and their properties.

It is quite clear that more research covering a greater number of particles, has to be carried out in order to fully understand the presence of defects in tcp alloys. The investigation started here in Lund will also continue - hopefully with the next generation of completely equipped instruments.

ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to Prof Sten Andersson for his constant encouragement, never-failing enthusiasm and support during the course of this work.

I am also deeply indebted to the following persons:

Prof Bengt Aurivillius for providing premises during the first part of this work.

Helén Ingesson, Ingrid Mellqvist, Lars Thell and Christer Jönsson for typing, drawing, computing and photographic work.

All my other colleagues who have provided a nice atmosphere and many helping hands over the years.

This work has partly been financed by the Swedish Natural Science Research Council.

REFERENCES

1. Friauf, J.B. Phys. Rev. 29, 34 (1927).
2. Friauf, J.B. J. Am. Chem. Soc. 49, 3107 (1927).
3. Hartmann, H., Ebert, F. and Bretschneider, O. Z. Anorg. Allg. Chem. 198, 116 (1931).
4. Laves, F. and Witte, H. Metallwirtschaft 14, 645 (1935).
5. Arnfelt, H. and Westgren, A. Jernkontorets Ann. 119, 185 (1935).
6. Bain, E.C. and Griffiths, W.E. Trans. Am. Inst. Min. Met. Eng. 75, 166 (1927).
7. Shoemaker, D.P. and Bergman, B.G. J. Am. Chem. Soc. 72, 5793 (1950).
8. Tucker, C.W. Science 112, 448 (1950).
9. Tucker, C.W. Acta Cryst. 4, 425 (1951).
10. Donohue, J. and Einsparr, H. Acta Cryst. B27, 1740 (1971).
11. Brink, C. and Shoemaker, D.P. Acta Cryst. 8, 734 (1955).
12. Shoemaker, D.P., Brink-Shoemaker, C. and Wilson, F.C. Acta Cryst. 10, 1 (1957).
13. Wilson, C.G., Thomas, D.K. and Spooner, F.J. Acta Cryst. 13, 56 (1960).
14. Brink-Shoemaker, C. and Shoemaker, D.P. Acta Cryst. 23, 231 (1967).
15. Gladyshevskij, E.I., Kripjakevich, P.I. and Skolozdra, R.V. Soviet Physics Doklady 12, 755 (1968); Structure Reports 32A, 57 (1967).
16. Brink-Shoemaker, C. and Shoemaker, D.P. Acta Cryst. B27, 227 (1971).
17. Manor, P.C., Brink-Shoemaker, C. and Shoemaker, D.P. Acta Cryst. B28, 1211 (1972).
18. Jarmoljuk, Ja.P., Kripjakevich, P.I. and Gladyshevskij, E.I. Structure Reports 35A, 50 (1970).

19. Kripjakevich, P.I. and Jarmoljuk, Ja.P. Dop. Akad. Nauk. Ukr. R.S.R. Ser. A, 10, 948 (1970); Structure Reports 37A, 70 (1971).
20. Kripjakevich, P.I. and Jarmoljuk, Ja.P. Dop. Akad. Nauk. Ukr. R.S.R. Ser. A, 36, 460 (1974); Structure Reports 43A, 73 (1977).
21. Jarmoljuk, Ja.P., Kripjakevich, P.I. and Melnik, E.V. Kristallografija 20, 538 (1975); Structure Reports 41A, 92 (1975).
22. Simon, A., Brämer, W., Hillenkötter, B. and Kullmann, H.-J. Z. Anorg. Allg. Chem. 419, 253 (1976).
23. Bergman, G. and Shoemaker, D.P. Acta Cryst. 7, 857 (1954).
24. Kasper, J.S. Theory of Alloy Phases, Amer. Soc. of Metals Symp. 264 (1956).
25. Frank, F.C. and Kasper, J.S. Acta Cryst. 11, 184 (1958).
26. Frank, F.C. and Kasper, J.S. Acta Cryst. 12, 483 (1959).
27. Cundy, H.M. and Rollet, A.P. Mathematical Models, Oxford, Clarendon Press, p 56 (1952).
28. Shoemaker, C.B. and Shoemaker, D.P. Developments in the Structural Chemistry of Alloy Phases, New York, Plenum Press, p 107 (1969).
29. Pearson, W.B. and Shoemaker, C.B. Acta Cryst. B25, 1178 (1969).
30. Hyde, B.G., Bagshaw, A.N., Andersson, S. and O'Keeffe, M. Defect Structures in Crystalline Solids. Ann. Rev. Mater. Sci. 4, 43 (1974).
31. Andersson, S. Structure and Bonding in Crystals, Vol II, Academic Press, New York, p 233 (1981).
32. Andersson, S. and Hyde, B.G. Z. Kristallogr. 158, 119 (1982).
33. Andersson, S. Angew. Chem. Int. Ed. Engl. 22, 69 (1983).
34. Andersson, S. J. Solid State Chem. 23, 191 (1978).
35. Andersson, S. and Stenberg, L. Z. Kristallogr. 158, 133 (1982).

36. Dickins, G.J., Douglas, A.M.B. and Taylor, W.H. *Nature*, 167, 192 (1951).
37. Kasper, J.S., Decker, B.F. and Belanger, J.R. *J. Appl. Phys.* 22, 361 (1951).
38. Holden, A.N. *Acta Cryst.* 5, 182 (1952).
39. Marcinkowski, M.J. and Miller, D.S. *Philos. Mag.* 7, 1025 (1962).
40. Allen, C.W., Delavignette, P. and Amelinckx, S. *Phys. Stat. Sol. (a)* 9, 237 (1972).
41. Kitano, Y., Komura, Y. and Kajiura, H. *Trans. Jpn. Inst. Met.* 18, 39 (1962).
42. Kitano, Y., Komura, Y. and Kajiura, H. *Acta Cryst.* A36, 16 (1980).
43. Wadsley, A.D. and Andersson, S. *Perspectives in Structural Chemistry*, Vol 3, John Wiley & Sons, p 1 (1970).
44. Andersson, S. and Hyde, B.G. *J. Solid State Chem.* 9, 92 (1974).
45. Wilson, C.G. and Spooner, F.J. *Acta Cryst.* 16, 230 (1963).
46. Ishimasa, T., Kitano, Y. and Komura, Y. *Jpn. J. Appl. Phys.* 19 (8), L483 (1980).
47. Ishimasa, T., Kitano, Y. and Komura, Y. *J. Solid State Chem.* 36, 74 (1981).
48. Ishimasa, T., Kitano, Y. and Komura, Y. *Phys. Stat. Sol.* 66, 703 (1981).
49. Ishimasa, T. *J. of Science of Hiroshima Univ.* A45 (1), 29 (1981).
50. O'Keefe, M.A., Self, P.G., Southwick, P.D. and Stobbs, W.M. *Electron Microscopy 1980*, 1, 264 (1980) *Proc. Seventh European Congress on Electron Microscopy*, Leiden 1980.
51. Southwick, P.D. and Stobbs, W.M. *J. Microsc.* 119, 169 (1980).
52. Andersson, S. and Wadsley, A.D. *Nature* 6, 581 (1966).

53. Kiessling, R. Acta Chem. Scand. 4, 146 (1950).
54. Cromer, D.T. Acta Cryst. B34, 913 (1978).
55. Hall, E.O. and Algie, S.H. Met. Rev. 11, 61 (1966).
56. Stenberg, L. and Andersson, S. Z. Kristallogr. 158, 205 (1982).

